AD-A244 030

NONCLASSI
SECURITY CLA

(2)

REPORT DOCUMENTATION PAGE

DTIC ELECTE JAN 06 1992 S D D

1a. REPORT SECURITY CLASSIFICATION Nonclassified	1b. RESTRICTIVE MARKINGS None
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for Public Release. Distribution unlimited.
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) FINAL REPORT	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION University of Massachusetts 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry / Lederle GRT 102A Amherst MA 01003	7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington VA 22217-5000
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research 8b. OFFICE SYMBOL (If applicable) ONR	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. N00014-87 / PROJECT NO. K-0464 / TASK NO. / WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)
Theoretical Investigations and Attempted Synthesis of Organic Magnetic Polymers and Oligomers.

12. PERSONAL AUTHOR(S) Paul M. Lahti

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
FINAL REPORT	FROM 6-1-87 TO 3-31-91	1991 Dec., 11	4

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Magnetic materials, polymers, radicals, information storage.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

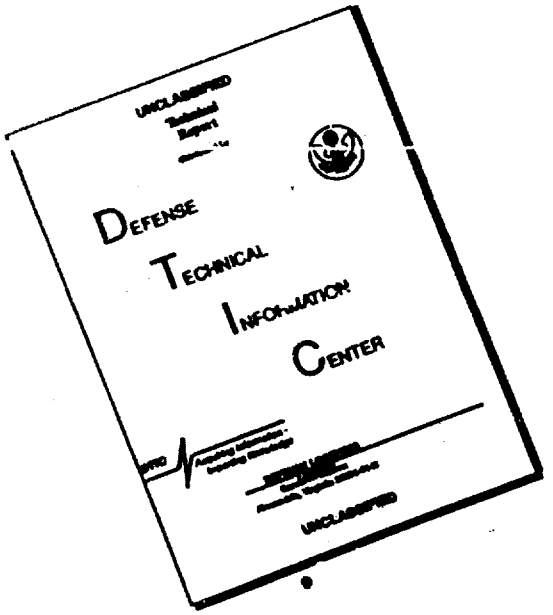
A final summary is given concerning the present state of attempts to generate very high spin organic molecules and polymers which possess ferromagnetic bulk properties. Methodology has been developed to predict the type of structures most likely to have such properties, and significant progress has been made toward photochemical generation of polyradicals in the solid state.

92-00205

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION NONCLASSIFIED
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Kenneth Wynne / Dr. JoAnn Milliken	22b. TELEPHONE (Include Area Code) 202-696-4410 / 22c. OFFICE SYMBOL ONR

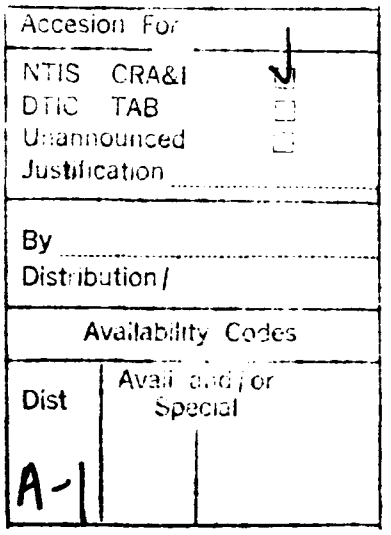
DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted. SECURITY CLASSIFICATION OF THIS PAGE

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

OFFICE OF NAVAL RESEARCH



CONTRACT N00014-87-K-0464

R & T Code
413c037

Final Project Report

THEORETICAL INVESTIGATIONS AND ATTEMPTED SYNTHESIS OF ORGANIC MAGNETIC POLYMERS AND OLIGOMERS

Paul M. Lahti

University of Massachusetts
Department of Chemistry
Amherst, MA 01003

THEORETICAL INVESTIGATIONS AND ATTEMPTED SYNTHESIS OF ORGANIC MAGNETIC POLYMERS AND OLIGOMERS

Paul M. Lahti

I. Brief Summary of Goals of Project:

This project was aimed at designing magnetic properties in new materials, particularly organic polyradicals. We desired to use semiempirical molecular orbital plus configuration interaction computational methods to predict what types of structural features are most important in maximizing desirable ferromagnetic exchange interactions within organic systems (intramolecular exchange). Once appropriate structural models were delineated by theory, we also aimed to develop a solid-state photochemical method to generate phenoxyl radical sites in a polymeric material. Use of a solid-state polyradical synthesis method would allow masking techniques for production of magnetic sites on a surface, and would minimize the kinds of radical quenching reactions that tend to reduce stability of radicals under free diffusion (solution) conditions.

II. Major Accomplishments of This Project:

(1) The use of the AM1 semiempirical computational model, with limited configuration interaction, gives excellent predictive capability in comparison to experimental results for the qualitative ground state multiplicity of organic diradical models [Tech. Rep. 3, 5, 6, 13, 15]. In addition, computed energy gaps between ground and excited states are in good agreement with ab initio quantum theoretical predictions, where such comparisons are available. The AM1-CI method is readily available through use of the AMPAC (version 2.10) program from the Quantum Chemistry Program Exchange at Indiana University.

(2) AM1-CI computations predict that several structural types of organic polyradicals should have ferromagnetically coupled exchange, for up to four or five-fold oligomers [Tech. Rep. 13, 15]. Geometric torsion effects that break conjugation can severely reduce exchange through a conjugated chain in some cases. Computations on model polyphenoxyl oligomer systems indicate that these are appropriate synthetic targets to achieve long-chain ferromagnetic coupling in a single polyradical chain.

(3) Experimentally, we have developed an entirely new, photochemical strategy for generating phenoxyl radicals [Tech. Rep. 7, 8, 11, 12, 14, 16, 17]. The method is based upon use of aryl oxalate derivatives, which are cheaply and easily synthesized. A peroxy-ester derivative gives very high quantum yields of products upon photolysis [Tech. Rep. 8, 11], but produces byproducts that are sufficiently reactive to destroy a substantial number of the desired phenoxyl radicals. In addition, the peroxy ester-based systems have limited thermal stabilty in several cases. Diaryl oxalates (DAOs) are thermally much more stable than the peroxy esters, give useful quantum yields of phenoxyl radicals, and show much high stability of phenoxyl radicals in rigid matrices upon warming [Tech. Rep. 16-18].

(4) Use of our model DAO methodology has been extended from small molecules, to functionalize pendant polyphenolic polymers. We have attached DAO photoactive groups to poly(4-hydroxy-styrene), and photolyzed at 77 K (-196°C) to produce a nonconjugated pendant polyphenoxyl radical [Tech. Rep. 18]. We find this method to possess high spin yields of radicals in sufficient proximity to exhibit antiferromagnetic coupling. The poly-DAO photochemical precursor polymer is

thermally stable for indefinite periods, is easy to make, and provides a method previous unavailable for the solid-state generation and study of organic polyradical materials.

III. Potential Future Directions:

Future extensions of the work described above will involve optimization of the quantum yield of DAO-related phenoxyl-generating chemistry, by use of different substituents on the DAO groups. We also must learn to make conjugated poly-DAO precursors, in order to achieve the most desirable and strong magnetism associated with intramolecular, conjugative exchange interactions. Finally, polymer processibility will be an important consideration, since our photochemical method allows only surface production of polyradicals (50-100 μm deep). Gamma-irradiation may eventually also be useful for polyradical-based production of permanent, write-once-read-many (WORM) types of materials.

IV. Listing of Research Personnel Involved in This Project:

Paul M. Lahti	Assistant Professor	Principal Investigator
David Modarelli	Ph. D. Student	Research Assistant
Frank Rossitto	Ph. D. Student	Research Assistant
Masaki Minato	Ph. D. Student	Research Assistant
Andrew Ichimura	Ph. D. Student	Research Assistant

Va. Bibliography of Publications Acknowledging ONR Support, Which Were Submitted as or Derived from Technical Reports:

A. S. Ichimura, A. R. Matlin, P. M. Lahti, "An Ab Initio Study of Methano and Ethano Bridged Derivatives of Oxyallyl.", *J. Am. Chem. Soc.*, **1989**, *110*, 2868-2875.

P. M. Lahti, A. S. Ichimura, J. A. Berson, "Properties of Organic Diradicaloid Molecules Predicted by Semiempirical Molecular Orbital Theory. A Practical Procedure.", *J. Org. Chem.*, **1989**, *54*, 958-965.

P. M. Lahti, A. S. Ichimura, "Computational Modeling of Pi-Conjugated Polyradicals.", *Mol. Cryst. Liq. Cryst.*, **1989**, *176*, 125-138.

P. M. Lahti, A. S. Ichimura, "Semiempirical Study of Electron Exchange Interaction in Organic High-Spin Pi-Systems. Classifying Structural Effects in Organic Magnetic Molecules.", *J. Org. Chem.*, **1991**, *56*, 3030-3042.

P. M. Lahti, "Theoretical Investigations of Pi-Conjugated Polyradicals as Models for Organic Magnetic Materials.", *A.C.S. Polym. Preprints*, **1990**, *31(1)*, 710-711.

M. Minato, P. M. Lahti, "Biphenyl-3,4'-dinitrene.", *J. Phys. Org. Chem.*, **1991**, *4*, 459-463.

D. A. Modarelli, P. M. Lahti, "Diaryl Oxalates as Convenient Unimolecular Sources of Aryloxyl Radicals.", *Chem. Comm.*, **1990**, 1167-1168.

D. A. Modarelli, P. M. Lahti, *J. Am. Chem. Soc.*, **1991**, *113*, 6329-6330.

D. A. Modarelli, F. C. Rossitto, P. M. Lahti, "Convenient Unimolecular Sources of Aryloxyl Radicals. I -- Aryloxyoxalyl Chlorides.", *Tet. Lett.*, **1989**, 4473-4476.

D. A. Modarelli, F. C. Rossitto, P. M. Lahti, "Convenient Unimolecular Sources of Aryloxyl Radicals. II -- Aryloxyoxalyl Tert-Butyl Peroxides.", *Tet. Lett.*, **1989**, 4476-4479.

D. A. Modarelli, F. C. Rossitto, M. Minato, P. M. Lahti, "Organic Polyradical Models for Organic Magnetic Materials.", *Mater. Res. Soc. Sympos. Proc.*, **1990**, 173, 83-88.

VIb. **Listing of Technical Reports During Project Period.**

1. P. M. Lahti, A. Ichimura, M. Kearley, D. Modarelli, "Electronically and Magnetically Unusual Materials.
2. P. M. Lahti, A. Ichimura, D. Modarelli, M. Kearley, "Non-Kekule Molecules -- Theory, Practice and Uses."
3. P. M. Lahti, A. S. Ichimura, "Computational Modeling of Pi-Conjugated Polyradicals."
4. D. A. Modarelli, F. C. Rossitto, P. M. Lahti, "Experimental Progress Toward Synthesis of Very High Spin State Organic Polyradicals."
5. P. M. Lahti, A. Ichimura, J. A. Berson, "Properties of Organic Diradicaloid Molecules Predicted by Semiempirical Molecular Orbital Theory. A Practical Procedure."
6. P. M. Lahti, A. S. Ichimura, "Computational Modeling of Pi-Conjugated Polyradicals."
7. D. A. Modarelli, F. C. Rossitto, P. M. Lahti, "Convenient Unimolecular Sources of Aryloxyl Radicals. I - Aryloxyoxalyl Chlorides." (preprint)
8. D. A. Modarelli, F. C. Rossitto, P. M. Lahti, "Convenient Unimolecular Sources of Aryloxyl Radicals. II - Aryloxyoxalyl Tert-Butylperoxides." (preprint)
9. A. S. Ichimura, P. M. Lahti, A. R. Matlin, "An Ab Initio Study of Methano and Ethano Bridged Derivatives of Oxyallyl."
10. P. M. Lahti, "Theoretical Investigations and Attempted Synthesis of Organic Magnetic Materials."
11. D. A. Modarelli, F. C. Rossitto, P. M. Lahti, "Convenient Unimolecular Sources of Aryloxyl Radicals. I - Aryloxyoxalyl Chlorides." (reprint)
12. D. A. Modarelli, F. C. Rossitto, P. M. Lahti, "Convenient Unimolecular Sources of Aryloxyl Radicals. II - Aryloxyoxalyl Tert-Butylperoxides." (reprint)
13. P. M. Lahti, A. S. Ichimura, "Computational Modeling of Pi-Conjugated Polyradicals."
14. D. A. Modarelli, F. C. Rossitto, M. Minato, P. M. Lahti, "Organic Polyradical Models for Organic Magnetic Materials."
15. P. M. Lahti, "Theoretical Investigations of Pi-Conjugated Polyradicals as Models for Organic Magnetic Materials."
16. D. A. Modarelli, P. M. Lahti, "Bis-Aryloxalates as Convenient Unimolecular Sources of Aryloxyl Radicals."
17. P. M. Lahti, D. A. Modarelli, "Solid State Photochemical Generation of Triplet Phenoxy-Phenoxy Radical Pairs."
18. P. M. Lahti, F. C. Rossitto, "Progress Toward Synthesis of Polymeric Polyradicals."
19. P. M. Lahti, D. A. Modarelli, F. C. Rossitto, M. Minato, "Investigations of Spin Coupling Mechanisms in Organic Systems."
20. M. Minato, P. M. Lahti, "3,4'-Biphenyldinitrene."